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REMARKS

Consideration of GB 933,127 (copy enclosed) in the instant prosecution is requested. The indication that this document – submitted along with the original filing has not been considered has been noted. Enclosed resubmitted is an additional copy of this document believed in proper form permitting its consideration.

The rejection of Claim 1 under section 112 is believed addressed and overcome by the present amendment.


Claims 1-9 are pending. All but Claim 4 stand rejected; Claim 4 indicated to be directed to allowable subject matter is objected to.

Claims 1-3 and 5-9 stand rejected under 35 U.S.C. 102(b) as anticipated by EP378104.

The present amendment limits the scope of the protection to that of Claim 4.

Believing the above represent a complete response to the Office Action and that the application is in condition for allowance, Applicants request the earliest issuance of an indication to this effect.

Respectfully submitted,

By 
Aron Preis
Attorney for Applicants
Reg. No. 29,426

Bayer MaterialScience LLC
100 Bayer Road
Pittsburgh, Pennsylvania 15205-9741
(412) 777-3814
FACSIMILE PHONE NUMBER:
(412) 777-3902
lo/PREIS/ap265

PATENT SPECIFICATION

933,127

NO DRAWINGS.

The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act, 1949, are ADOLF STEINHOFER, RUDOLF POLSTER and HERBERT FRIEDERICH, Citizens of Germany and residents, respectively, of 11 Wolframstrasse Ludwigshafen/Rhein, Germany; 165 Bergstrasse, Heidelberg, Germany; and 8 Bayou Road, Lake Jackson, Texas, United States of America.

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Index at Acceptance :—Class 2(6), P2(D1A:K7:T2F), P4(D3B1:K7:T2F), P6(D1:K7:T2F), P7A, P7D(1A:1B:1X:2A1:2A2B:2A4:2B:3), P7K(2:4:6:7:8:11), P7P(1B:2X), P7T2F, P8D(2A:2B2:3A:3B), P8(K7:T2F), P11(D2A:K7:T2F).

International Classification :—C08f.

COMPLETE SPECIFICATION.

Production of Polymers of Vinylcyclohexane.

We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of Ludwigshafen/Rhein, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of polymers of vinylcyclohexane by hydrogenation of styrene polymers.

It is known that by catalytic pressure hydrogenation at temperatures above 200° C. of polystyrenes having molecular weights below 10,000 it is possible to convert them into polyvinylcyclohexanes the softening point of which is higher than that of the initial product. In spite of the inexpensiveness of polystyrene, such hydrogenated polystyrenes have not hitherto achieved any technical importance because hydrogenation of the high molecular weight polystyrenes is attended by marked decrease in the molecular size so that very brittle polyvinylcyclohexanes are formed which are unsuitable as raw materials for plastics.

It has been proposed to hydrogenate polystyrene in the presence of unsupported nickel catalysts obtained by hydrogenating decomposition of nickel oxalate. Polystyrenes obtained by this method are however only partly hydrogenated.

[Price

It is also known that vinylcyclohexane can be polymerized stereospecifically to high molecular weight substances. Identical substances are obtained by hydrogenation of stereoregular poly-*p*-chlorostyrene. However, such polyvinylcyclohexanes have a very high crystallite melting point. They therefore cannot be processed by the conventional methods for thermoplastic substances and consequently are not suitable as raw materials for plastics.

The object of the invention is to provide a process for the production of polymers of vinylcyclohexane with molecular weights between 10,000 and 2,000,000.

This object is achieved by hydrogenating a homopolymer, copolymer or graft polymer of styrene or a mixture of polymers containing polystyrene and having molecular weights between 10,000 and 2,000,000 in the liquid phase, with hydrogen at temperatures between 50° and 270° C. and under pressure between 10 and 100 atmospheres in the presence of supported catalysts which contain between 0.01 and 95% by weight of metal of group VIII of the Periodic System with an atomic weight exceeding 58.

The Periodic System referred to in this Specification is that given in the "Handbook of Chemistry and Physics", 40th Edition, pp. 448/9.

Polymers of vinylcyclohexane prepared by the process according to the present invention are distinguished from polymers of styrene by their higher thermal stability, aging resistance, and light resistance, lower density and hence increased economy with constant transparency.

Soluble polymers of styrene, including homopolymers, copolymers and graft polymers, and also polymer mixtures containing polystyrene and having molecular weights between 10,000 and 2,000,000 are suitable as initial materials for the process. The average molecular weight of the initial material may vary within wide limits and depends on the desired molecular weight of the vinylcyclohexane polymer. The molecular weight of the initial material is determined to some extent by the requirement that the substance to be hydrogenated must either be present in molten form or be soluble in the solvent used at the reaction temperature. The molecular weight will be above 10,000 and not above 2,000,000. Vinylcyclohexane polymers having especially valuable properties are obtained when the molecular weight of the initial material is within the range 50,000 to 1,000,000 and especially between 150,000 and 800,000.

The following may be given as examples of homopolymers of styrene: polystyrene prepared by thermal polymerization of styrene, polystyrene prepared by ionic polymerization using alkali metals, and stereoregular polystyrene obtainable for example by polymerization of styrene using aluminum or aluminum alkyls and titanium halides. Polystyrene prepared with radical-forming substances in emulsion or suspension is also suitable as initial material. Examples of components in copolymers are butadiene, isobutylene, vinyl toluene, α -methylstyrene, divinylbenzenes, ethylene, propylene, acrylic esters, methacrylic esters, vinyl esters, vinyl ethers, acrylonitrile, methacrylonitrile, N-vinylcarbazole; mixtures of the said polymers and/or copolymers may also be used.

Especially useful products are obtained from copolymers of styrene with α -methylstyrene and vinyl toluene, which contain at least 50% by weight of styrene in polymerized form.

Hydrogenation of the initial material is carried out in the liquid phase. Thus either a melt of the polymer or a solution of the polymer may be treated with hydrogen.

Suitable solvents are aliphatic and cycloaliphatic hydrocarbons; aliphatic and cycloaliphatic saturated ethers or mixtures thereof may however also be used. For example a mixture of cyclohexane and tetrahydrofuran has proved to be especially suitable. Alcohols and aromatic hydrocarbons may be used in addition to the said solvents.

For reasons of economy, the concentration of the initial polymers in the solution should be as high as possible. It depends on the nature and the molecular weight of the initial material. If it is desired to keep the polymer in solution in the cold, the concentration is in general between 5 and 25% by weight. One embodiment of the process according to this invention comprises adding to the polymer only sufficient solvent to form a flowable solution at the reaction temperature. Substantially smaller amounts of solvent, for example 10 to 300% of solvent with reference to the polymer, are then necessary depending on the nature of the polymer and solvent.

The catalysts for the process are supported catalysts which as active component contain a metal of group VIII of the Periodic System with an atomic weight between 58 and 196. Especially suitable are the metals nickel, cobalt, ruthenium, rhodium, palladium and platinum. Suitable carriers are porous substances which are stable under the process conditions, and on which the metals can be applied in very fine distribution, such as carbon, aluminum oxide, pumice, kieselguhr, silica gel and other porous silicate materials. The supported catalysts contain between 0.01 and 95% advantageously between 0.1 and 85% by weight, of the active metal. Promoters, for example chromium, copper or manganese in the case of nickel and cobalt catalysts, are often advantageous to increase activity.

The reaction temperature to be used depends on the catalyst. The range from 50° to 270° C. is applicable; the temperature range between 70° and 180° C. is preferred. For example with nickel on aluminum oxide it is advantageous to work at 160° to 170° C., with cobalt on silicate carriers at 110° to 150° C., whereas for catalyst which contain 1% by weight of rhodium on aluminum oxide a temperature from 80° to 120° C. is suitable.

In principle the hydrogenation can be carried out at atmospheric pressure, but long residence periods favor degradation of the macromolecules. In order to achieve a satisfactory hydrogenation rate, increased pressure is chosen, for example between 10 and 1000 atmospheres. The pressure range between 150 and 750 atmospheres is preferred.

The process may be carried out batchwise or continuously. In batch operation, the reaction period is usually between 1 and 5 hours. In a continuous system, the reaction period is considerably shorter; it is influenced by the size of the reaction vessel. For continuous operation, use may be made of the trickling system or the system whereby the reactants are introduced into the liquid phase from the bottom, both systems

- with rigidly arranged catalysts, or of a system with a suspended catalyst which may for example be recycled. The catalyst is separated from the solution after the hydrogenation and the polymer recovered from the solution, which may have been further purified in conventional manner, for example by precipitation by means of precipitants or by separating the solvent by distillation.
- The full advantage of the process according to this invention is only achieved when all three double linkages of the aromatic nucleus are hydrogenated. When the initial material is only partly hydrogenated, the substances formed have softening points which as a rule are between that of the initial material and that of the hydrogenated polystyrene. Moreover, partially hydrogenated substances exhibit unsatisfactory transparency.
- There is no molecular degradation under the process conditions. The hydrogenated product has practically the same degree of polymerization as the initial material.
- The vinylcyclohexane polymers obtained in almost theoretical yields are excellent raw materials for plastics, whose Vicat dimensional stability under heat may reach 140° C. They may therefore be regarded as absolutely stable to boiling water. They exhibit increased stability as compared with polystyrene also at a temperature above the softening point. They have the excellent transparency of the initial material. In the case of dull or cloudy polymer mixtures, transparency is usually increased by the hydrogenation.
- The above-mentioned properties make pure polyvinylcyclohexane suitable as a raw material for plastics for the production of completely transparent moulded articles having dimensional stability even at high temperatures. It is remarkable that the density is 0.94 to 0.95 which is much lower than that of polystyrene. The economy of polyvinylcyclohexane as a raw material for plastics is thus higher than that of polystyrene.
- Higher temperature resistance is also the characteristic property in the case of hydrogenated copolymers and graft polymers and also of polymer mixtures.
- The invention is illustrated by, but not limited to the following examples, in which parts are by weight. Molecular weights given are determined by light scattering measurement. Vicat dimensional stability under heat is measured according to DIN 57,302.
- EXAMPLE 1.**
- 50 parts of a polystyrene ("polystyrene IV", see H. Ohlinger, *Polystyrol*, Springer-Verlag (1955), page 62) and having a molecular weight of about 600,000 and a Vicat dimensional stability under heat of 90° C. is dissolved in a mixture of 100 parts of tetrahydrofuran and 1200 parts of cyclohexane and hydrogenated in the presence of 50 parts of a catalyst containing 75% of nickel and 25% of kieselguhr at 165° C. and 200 atmospheres hydrogen pressure for four hours. The catalyst is then filtered off from the polymer solution, the solution concentrated to a polymer content of 20% and the polymer precipitated in twice the volume of methanol. The precipitated polyvinylcyclohexane is filtered off by suction and dried at 105° C. in a drying cabinet. 51 parts of polyvinylcyclohexane is obtained having a molecular weight of about 610,000 and a Vicat dimensional stability under heat of 138° C. Analysis of this polyvinylcyclohexane gives the following results:—
- C=87.2% H=12.7%
- A sample pressed into sheets is completely transparent. A density of 0.95 g/cc is determined on this sample.
- EXAMPLE 2.**
- 50 parts of a styrene bulk polymer having a molecular weight of 300,000 and a Vicat dimensional stability under heat of 90° C. is dissolved in a mixture of 100 parts of tetrahydrofuran and 850 parts of cyclohexane and 50 parts of a powdered catalyst containing 1% of rhodium on aluminum oxide is added. The mixture is hydrogenated in an autoclave at 120° C. and a pressure of 300 atmospheres of hydrogen for three hours. After working up the product as described in Example 1, 52 parts of polyvinylcyclohexane is obtained having a molecular weight of 320,000 and a Vicat dimensional stability under heat of 135° C.
- EXAMPLE 3.**
- 50 parts of a polystyrene prepared by suspension polymerization with a molecular weight of 300,000 and a Vicat dimensional stability under heat of 100° C. is dissolved in a mixture of 100 parts of tetrahydrofuran and 850 parts of cyclohexane, a catalyst consisting of 75% of nickel and 25% of kieselguhr is added and hydrogenation effected for three hours at 160° C. and a hydrogen pressure of 200 atmospheres. After working up the product in the way described in Example 1, 49 parts of a polyvinylcyclohexane is obtained having a molecular weight of 300,000 and a Vicat dimensional stability under heat of 135° C. A density of 0.95 g/cc is determined.
- EXAMPLE 4.**
- 50 parts of polystyrene prepared by emulsion polymerization and having a Vicat dimensional stability under heat of 100° C.

and a molecular weight of about 800,000 is dissolved in a mixture of 150 parts of tetrahydrofuran and 900 parts of cyclohexane, and 50 parts of a powdered catalyst containing 10% of nickel and 0.1% of rhodium on aluminium oxide is added. The mixture is hydrogenated for four hours at 160° C. and a hydrogen pressure of 200 atmospheres. After the product has been worked up in the way described in Example 1, 51 parts of polyvinylcyclohexane is obtained which has a Vicat dimensional stability under heat of 135° C.

EXAMPLE 5.

15 15 parts of the styrene bulk polymer described in Example 2 is dissolved in 300 parts of cyclohexane and 20 parts of a powdered catalyst consisting of 100 parts of nickel, 20 parts of manganese, 10 parts of aluminium oxide and 15 parts of kieselguhr is added. The mixture is hydrogenated in an autoclave at 130° C. and a hydrogen pressure of 200 atmospheres for three hours. After the product has been worked up as described in Example 1, 15 parts of polyvinylcyclohexane is obtained having a molecular weight of 300,000 and a Vicat dimensional stability under heat of 137° C. Analysis of the polyvinylcyclohexane gives the following results:—

C=81.1% H=12.9%

EXAMPLE 6.

300 parts of the styrene bulk polymer described in Example 2 is dissolved in a mixture of 350 parts of cyclohexane and 350 parts of decahydronaphthalene and 70 parts of a powdered catalyst consisting of 100 parts of cobalt, 15 parts of manganese, 10 parts of copper and 110 parts of kieselguhr is added. The mixture is hydrogenated in an autoclave at 150° C. and a hydrogen pressure of 100 atmospheres for six hours. The reaction product is diluted with tetrahydrofuran to a polymer content of about 15%. The catalyst is filtered off from the polymer solution and the polymer precipitated in twice the volume of methanol. The precipitate is worked up as described in Example 1 and 314 parts of polyvinylcyclohexane is obtained having a molecular weight of 330,000 and a Vicat dimensional stability under heat of 136° C. Analysis of this polyvinylcyclohexane gives the following results:—

C=87.2% H=12.8%

EXAMPLE 7.

300 parts of the styrene bulk polymer described in Example 2 is dissolved in 700 parts of cyclohexane and 70 parts of a powdered catalyst consisting of 100 parts of

cobalt, 15 parts of manganese, 10 parts of copper, 2.5 parts of cerium oxide and 110 parts of kieselguhr is added. The mixture is hydrogenated in an autoclave at 140° C. and a hydrogen pressure of 200 atmospheres for 3½ hours. The reaction product is diluted with tetrahydrofuran to a polymer content of about 15%. Catalyst is then filtered off from the polymer solution and the polymer precipitated in twice the volume of methanol. The precipitate is worked up as described in Example 1 and 315 parts of polyvinylcyclohexane is obtained. The molecular weight is 310,000 and the Vicat softening point is 133° C.

EXAMPLE 8.

15 parts of a polystyrene containing 10% of polybutadiene is dissolved in a mixture of 255 parts of cyclohexane and 30 parts of benzene, and 10 parts of a powdered catalyst containing 1% of rhodium on aluminium oxide is added. The mixture is hydrogenated in an autoclave at 120° C. and a hydrogen pressure of 200 atmospheres for four hours. The product is worked up as described in Example 1 and 13 parts of a polymeric hydrogenation product is obtained which has a Vicat dimensional stability under heat of 133° C.

EXAMPLE 9.

12 parts of the polystyrene described in Example 2 is dissolved in 388 parts of cyclohexane. 50 parts of the catalyst described in Example 6 is added. The mixture is hydrogenated for eleven hours at 150° C. and a hydrogen pressure of 20 atmospheres. The product is worked up as described in Example 1 and 11 parts of a polyvinylcyclohexane obtained whose Vicat dimensional stability under heat is 139° C. Analysis of this product gives the following results:

C=86.9% H=12.9%

EXAMPLE 10.

50 parts of a copolymer containing 75% of styrene and 25% of α -methylstyrene and having a Vicat dimensional stability under heat of 102° C. is dissolved in 950 parts of cyclohexane and hydrogenated for 2½ hours in an autoclave at 150° C. and a hydrogen pressure of 200 atmospheres in the presence of 50 parts of the catalyst described in Example 6. The product is worked up as described in Example 1 and 48 parts of hydrogenated polymer is obtained having a Vicat dimensional stability under heat of 151° C.

EXAMPLE 11.

375 parts of the polystyrene described in Example 2 is intimately mixed with 125 parts of decahydronaphthalene and 100 parts of the catalyst described in Example 6 and

the mixture hydrogenated for four hours in an autoclave at 160° C. and a hydrogen pressure of 200 atmospheres. The reaction product is worked up as described in Example 6. A polyvinylcyclohexane having a Vicat dimensional stability under heat of 136° C. and a molecular weight of 300,000 is obtained in almost quantitative yield. Analysis of this polymer gives the following results:—

10 C=87.0% H=12.8%

WHAT WE CLAIM IS:—

1. A process for the production of vinylcyclohexane polymers having molecular weights of between 10,000 and 2,000,000, wherein a homopolymer, copolymer or graft polymer of styrene or a mixture of polymers containing polystyrene and having molecular weights of between 10,000 and 2,000,000 is hydrogenated in liquid phase with hydrogen at temperatures between 50° and 270° C. and under a pressure between 10 and 1000 atmospheres in the presence of

a supported catalyst which contains between 0.01 and 95% by weight of a metal of group VIII of the Periodic System with an atomic weight exceeding 58. 25

2. A process as claimed in Claim 1 in which the hydrogenation is carried out at a temperature between 70° and 180° C.

3. A process as claimed in Claims 1 and 2, wherein the hydrogenation is carried out at a pressure between 150 and 750 atmospheres. 30

4. The process for the production of vinylcyclohexane polymers substantially as described in any of the foregoing examples. 35

5. Vinylcyclohexane polymers when obtained by the process claimed in any of Claims 1 to 4.

J. Y. & G. W. JOHNSON,
Furnival House,
14—18 High Holborn,
London, W.C.1,
Chartered Patent Agents,
Agents for the Applicants.